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Characterization of urban pollution in two cities of the Puglia region in Southern Italy using field measurements and air quality (AQ) model approach

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ABSTRACT

Passive air sampling (PAS) consisting of polyurethane foam (PUF) disks were deployed simultaneously over four periods of 2–5 months at four locations in urban and sub–urban sites of Bari and San Vito Taranto in Southern Italy. The purpose of the study was to characterize the urban pollution for two groups of semi volatile organic compounds (SVOCs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), by using two different approaches consisting of PAS–PUF and air quality models (Flexible Air quality Regional Model, FARM). The concentrations in the air ranged from 20 to 200 pg m^{-3} for PCBs and from 5 to 48 ng m^{-3} for PAHs with the highest concentrations being detected at Bari center. PCB composition was dominated by the 3–Cl congeners (periods 1 and 2) and by 5–Cl (periods 3 and 4). PCB–28 and –37 were the most abundant congeners during the four periods. The PAHs profile was dominated by the 3–ring (70±6)%, with phenanthrene alone accounting for (49±2)%. On a seasonal basis opposite patterns were observed for PCBs and PAHs showing high PCB concentrations during the warm periods, period 3: summer and 2: spring, while PAHs were found during cool periods, period 4: autumn, and 1: winter. The results obtained from the application of the FARM model, during 2010, and limited to period 4 in this study, showed similar estimated levels for PCBs indicating a good performance for PCB modeled concentrations whilst for benzo[*b*]fluoranthene (B[b]F) the results showed a less better agreement. This study represents one of the few efforts at characterizing PCBs and PAHs compositions in ambient air in southern Italy and also represents one of the preliminary attempts at using PAS–PUF to give more insight into a modeling prediction in Italy. These results also provide useful information for the future development of the FARM model.

Keywords: *Passive air sampling, SVOCs, urban sites, AQ models, FARM*

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1. Introduction

Urban areas are characterized by intense emissions from motor–vehicles traffic and industrial activities. In these environments emitted species, such as semi–volatile organic compounds (SVOCs) may accumulate enhancing environmental risk and health problems related to human exposure to such pollutants in these areas. SVOCs include a variety of compounds such as dioxins, organochlorine pesticides, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) (He and Balasubramanian, 2010). International efforts to control the production, the emission, and the use of SVOCs have been established by the United Nations Economic Commission for Europe (UNECE) with the Convention on Long Range Transboundary Air Pollution (CLRTAP) (1998) and by the United Nations Environment Programme (UNEP) with the Stockholm Convention (SC) (2001). Italy has underwritten the SC since 2001 and the UNECE Protocol since 2003. However, Italy is the only country in Europe that has not yet ratified the SC concerning POPs.

Breivik et al. (2007) estimated PCBs global production at ~1.3 million tons with more than 70% comprising tri–, tetra– and penta–PCBs and with almost 97% of the global historical use of PCBs occurring in the Northern Hemisphere. In Italy, the production of PCBs began in 1958 and ended in 1983 with a cumulative production of approximately 31 092 tons (Breivik et al., 2007).

PAHs are unavoidable by–products of any kind of combustion, mainly incomplete combustion, (Jaward et al., 2004a). Consequently, elevated levels in the range of ng m^{-3} are typically found in urban environments, where their sources are almost exclusively anthropogenic (Hafner et al., 2005).

In Italy PCBs and PAHs have been studied mostly by using active air sampling and mainly in the particulate phase. For instance, some investigations have reported levels of PCBs in air in sub–alpine northern Italy (21 to 72 pg m^{-3}) (Castro–Jimenez et al., 2009) and air concentrations of PAHs in Florence (Lodovici et al., 2003), in Prato (Cincinelli et al., 2007). Recently, Amodio et al. (2009) reported levels of PAH in the cities of Bari and Taranto, and Di Filippo et al. (2010) in the city of Taranto, showing annual average air concentrations (ng m^{-3}) of ~3.2 (ranging from 0.52 to 15) and from 1.8 to 69.7 (3.8 to 69.7 winter, and 1.8 to 8.2 summer), respectively. However, previous studies have focused on the particulate phase and on the highest molecular weight PAHs.

During the last decade, passive air sampling (PAS) has become increasingly used as a time integrating tool for a wide range of compounds. PAS consisting of polyurethane foam disk (PUFs disk)

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is a very cost effective tool for monitoring POPs because it is easy to handle and does not require electricity. Previous studies based on a local, regional and continental scale have used PUF disks as PAS (PAS–PUF) (Pozo et al., 2009; Halse et al., 2011). Recently, in Italy, Estellano et al. (2012) have reported levels of PCBs, PBDEs, OCPs and PAHs, at different land use sites, using PAS–PUF in the Tuscany region.

In Italy, there is still a lack of information about the characterization of urban pollution for SVOCs. This information is needed to assess human exposure particularly in highly populated urban centers. One way to bridge this gap is to estimate the concentrations of atmospheric pollutants by using chemical transport models (CTMs). CTMs are helpful tools for understanding the environmental fate and source–receptor relationships because they accurately represent the main processes affecting pollutants in the atmosphere such as emissions, dispersion, chemical transformation and depositions. CTMs have been widely used in Italy (e.g. Gariazzo et al., 2007; Lonati et al., 2010) to assess the air quality in areas not covered by measurements and to evaluate the effects of emission control strategies. In this context the Italian Ministry of Environment has funded the scientific project MINNI (National modelling system for supporting the international negotiation process on air pollution and assessing air quality policies at national/regional level; Zanini et al., 2005) (http://www.minni.org/). The Air Quality Modeling System (AQMS) of MINNI is based on the Flexible Air quality Regional Model (FARM) (Silibello et al., 2008) that has been recently extended to POPs. A summary of the efforts to simulate the atmospheric processes involving POPs in CTMs can be found in Silibello et al. (2012) and references therein.

In this study two different approaches were used to characterize urban pollution in two cities of the Puglia region in Italy. The first approach consisted in using PAS–PUF to assess the air concentrations of PCBs and PAHs (field measurements) and the second by predicting their air concentrations using a CTM. Levels and seasonal variations of selected PCBs and PAHs were also assessed. Measured concentrations in the air for some of the PCBs and B[b]F were compared with obtained FARM predictions. This work provides new information on PCBs and PAHs composition in the urban atmosphere in the Southern Italy and contributes, in a preliminary attempt, to complement modeling predictions with field measurements in Italy.

2. Material and Methods

2.1. Sites

Four locations were selected in the Puglia region in southern Italy, three of them in urban sites in the city of Bari, and one in a sub–urban site in San Vito Taranto, southern fraction of the city of Taranto (see the Supporting Material, SM, Figure S1). Description of the sampling areas and prevalent meteorological conditions are given in the SM, Text S1.

PUF disks were deployed, one sampler per site, for four sampling periods of approximately 2–5 months each (see the SM, Table S1): Period 1: from January to April 2009 (winter), Period 2: from April to June 2009 (spring), Period 3: from June to September (summer), and Period 4: from September 2009 to February 2010 (autumn). Detailed information regarding latitude and longitude co–ordinates, deployment time and temperatures are presented in the SM, Table S1.

2.2. Sampler preparation, deployment and analysis

Details on preparation, deployment and analysis procedures have been reported elsewhere (Pozo et al., 2009; Estellano et al., 2012). Briefly, PUF disk samples were extracted in Soxhlet for 24 h using petroleum ether (300 ml); extracts were concentrated to 0.5 ml and solvent exchanged to isooctane. Mirex (100 ng) was added as internal standard. The analysis of PUF disk extracts was carried out by gas chromatography–mass spectrometry (GC–MS) using positive electron impact–selected ion monitoring. PUF disk samples were analyzed for 15 PAHs and for a mixture of 28 PCBs. The details about the instrumental conditions and methods are presented in the SM Texts S2.

Shoeib and Harner (2002) provided the calibration for the PUF disk passive samplers for non–polar hydrophobic chemicals. Briefly, the uptake by passive sampling media has been shown to be controlled by the air–side mass transfer coefficient, k_A (m h^{-1}), which is a weak function of temperature (Shoeib and Harner, 2002; Pozo et al., 2004).

2.3. Derived air sample volumes

Information on sampler performance and methods to ascertain air concentrations were reported previously (Shoeib and Harner, 2002; Pozo et al., 2004). Briefly, air concentrations for the target chemicals were derived from the amount accumulated in the PUF disk (ng $sampler^{-1}$) and the effective air volume. In order to estimate the effective air volume, Equation (2) from Shoeib and Harner (2002) and Pozo et al. (2004) was used which considers the full uptake profile – linear phase and the plateau phase.

$$V_{air}=(K'_{PUF-A})\times(V_{PUF})\times\{1-\exp[-(Time)\times(k_A)/(K'_{PUF-A})/(D_{FILM})]\} \quad (1)$$

where: K'_{PUF-A} is the partition coefficient between the passive air sampling media and the air (calculated from octanol–air partition coefficient K_{OA}); V_{PUF} is the volume of the PUF disk (cm^3); *Time* is the deployment time (days) of the PUF; k_A is the air–side mass transfer coefficient=R/A_{PUF} (Surface Area of PUF in cm^2); and $D_{FILM}=V_{PUF}/A_{PUF}$ is the "effective" thickness. The plateau phase may be relevant for the more volatile PAHs (acenaphthylene to chrysene) with lower K_{OA} values that may approach equilibrium during deployment, resulting in reduced sample air volumes.

Previous studies have reported that PUF disks may be used for sampling the gas phase (in which the lower molecular weight (LMW) PAHs are mainly found), and also be able to sample ambient particles (where the higher molecular weight (HMW) PAHs are mainly associated) (Chaemfa et al., 2009). Klanova et al. (2008) reported in the background site of Kosetice that only 10% of ambient particles are captured by PUFs, showing a reduced sampling rate (R) compared to the LMW PAHs. However, other studies found no discrimination in the HMW PAHs R–value, for instance: in tropical (He and Balasubramanian, 2010), or in industrial/urban sites (Harner et al., 2013). In the present study air volumes were calculated using a R–value of ~4 m^3 d^{-1}, based on previous studies (Pozo et al., 2009) and that resulted in sample air volumes of approximately 200 m^3 to 600 m^3 for PCBs and 50 m^3 to 600 m^3 for PAHs, depending on the length of deployment periods, average temperatures, and the physio–chemical proper-ties of the molecules (see the SM, Table S2 and S3).

2.4. Quality assurance/quality control (QA/QC)

The procedures described above were checked for recoveries and reproducibility. Procedural blanks (solvent blanks) were analyzed for QA/QC purposes. Prior to air samples extraction, three analytical blanks were prepared using the same extraction and clean–up procedure. Prior to extraction all PUF disks were spiked with recovery standards consisting of ^{13}C PCB–105 (99%, Cambridge Isotope Laboratory) and phenanthrene–d_{10} (99%, Supelco Analytical). A solvent blank was analyzed every 15 samples to check the response of the GC–MS.

Instrumental detection limits (IDL) were calculated using the same approach reported in Estellano et al. (2012) and Pozo et al. (2012). The MDL were defined as the average field and laboratory

blanks (n=4) plus three standard deviations (SD). If target compounds were not detected in blanks, ½ of the IDL value was substituted for the MDL. The MDL values for each target compound are reported in the SM Tables S2 and S3.

Average surrogate method recoveries were satisfactory (70±10)% for ^{13}C–PCB–105 and (75±10)% for phenanthrene–d_{10}. This result coupled with previous external recovery checks (Estellano et al., 2012; Pozo et al., 2012) for target compounds indicated that the analysis method was satisfactory and that recovery correction of the data was not needed. Solvent (method) blank values for individual PCB congeners were low and not detectable for higher molecular weight PCB.

2.5. Air quality modeling system (AQMS)

The AQMS QualeAria (http://www.aria–net.eu/QualeAria/index_en.html) implements state–of–the–art techniques to describe physical and chemical processes involving pollutants in the atmosphere (e.g. emissions, transport, dispersion, deposition and chemical reactions). The main aim of the modeling system is to simulate regional scale air pollution over the Italian peninsula starting from national and European emission inventories, synoptic scale weather analysis and global scale air quality levels. It has been developed within the research project FUMAPEX, funded by the European Commission within the 5th Framework Programme, and the COST Action ES0602 collaboration framework.

The AQMS is constituted by the following modules whose connections are depicted by Figure S10 (see the SM):

- RAMS (Cotton et al., 2003) prognostic meteorological model for synoptic weather downscaling and description of local scale atmospheric flows,
- An interface module (GAP/SURFPRO) to match meteorological fields produced by RAMS to FARM nested computational domains describe atmospheric turbulence and define dispersion parameters,
- An emission processor (EMMA) to provide gridded pollutants emissions starting from European and national inventories,
- Eulerian chemical transport model FARM to simulate transport, dispersion, deposition and chemical reactions of atmospheric pollutants.

The AQMS is applied simultaneously to a background domain including a large fraction of continental Europe and the Mediterranean basin and to a target area including the whole Italian Peninsula (see the SM, Figure S10). Computational grid nesting techniques allow us to take into account the effects of sources located outside the target domain and large scale processes that influence the air quality at national and urban scales (e.g. photochemical smog).

2.6. Statistical analysis

In order to assess the seasonal variations, statistical analysis was developed using box and whisker plots (see the SM, Figures S4). The lines within the box represent the mean; the box itself contains the median±the standard error; the whiskers at either end of the box indicate the interval non–outlier.

Principal Component Analysis (PCA) is a multivariate statistical method and was performed using the XLSTAT program. The analysis has been described elsewhere (Pozo et al., 2012). Briefly: Prior to performing analysis, the data was natural log transformed. Spatial arrangement of compounds was analyzed to understand relationships among the target compounds. Varimax rotation was used as the rotation method for PCA analysis.

3. Results and Discussion

3.1. PCBs

Figure 1 presents the concentrations in the air of the PCB congener composition during the four sampling periods. Of the 28 PCB congeners that were analyzed 26 were frequently detected (see the SM, Table S2). $\sum_{26}$PCB concentrations (pg m^{-3}) ranged from 30 to 200 (80±50) (Figure 1, Table S2). The highest PCBs concentra-tions (pg m^{-3}) were detected at Bari Centre (200), followed by Bari East (180), during period 3 and 2, respectively. These values are similar to results reported at other urban sites in Tuscany region [at Piombino (310) and Prato (270)] (Estellano et al., 2012); however, our results were lower than those reported in other selected urban areas in north–central Italy (~1 600 pg m^{-3}) (Jaward et al., 2004b), in Africa (500 pg m^{-3} to 1 ng m^{-3}) (Klanova et al., 2009) and in urban sites investigated under the GAPS Network (~300 to 600 pg m^{-3}) (Pozo et al., 2009). These differences are most likely due to the influence of the wind and the industrial areas of the cities of Bari and Taranto probably do not significantly impact the sampling sites (more discussion is given in the next section).

The PCB composition was dominated by the 3–Cl congeners during the periods 1 (58±7)% and 2 (41±35)% and by 5–Cl during the periods 3 (45±20)% and 4 (35±4)% (see the SM, Figure S5). Similar PCB composition dominated by middle–range molecules was also observed in other studies across the Tuscan region by Estellano et al. (2012) and across Europe by Jaward et al. (2004b) and Halse et al. (2011). This suggests that light to middle PCBs are more evenly distributed in the sampling sites in comparison to the heavier ones.

The most abundant individual PCBs congeners were PCB–37, –28, –52, –101 and –95, which contributed between 6 to 30% to the average concentration of $\sum_{26}$PCB, respectively (see the SM, Table S2). These results are similar to the abundance of individual PCBs found by Halse et al. (2011) across Europe, citing PCBs–52, –28, –101 and –153 as the most abundant congeners.

Based on the loading plot of the PCA for PCBs, results showed differences in the congener pattern among all sites and periods (see the SM, Figure S6). The first component and second compo-nent explained, respectively, 54% and 26% of the total variance in period 1; 48% and 38% in period 2; 46% and 43% in period 3; and 49% and 43% in period 4 (see the SM, Figure S6). These values could be associated with the two main sources of PCBs in Italy that are production processes (41%) and energy production (31%) (see the SM, Table S4). The PCA also groups the sampling sites according to similarity or differences in PCB composition. During the four sampling periods, the sites differ substantially from each other, with the exception of period 1, where the sampling sites at Bari south and at Bari east were closely grouped. Wind directions during those specific sampling periods might have influenced the results. Furthermore, these results highlight the large variability of the PCB mixture in air (and potential related sources) in Bari and San Vito Taranto sites (see the SM, Table S4).

3.2. PAHs

Figure 2 presents concentrations of PAHs in air during the four sampling periods. Of the 15 PAH analyzed only 10 compounds were routinely detected (see the SM, Table S3). The PAHs concentrations (ng m^{-3}) ranged from 5 to 46 (20±11) (Figure 2, Table S3). The highest concentrations (ng m^{-3}), were detected at Bari center (46). PAH levels detected in this study are similar to the average air concentrations of Σ_{15}PAHs (ng m^{-3}) found in the Tuscan region (21±34) (Estellano et al., 2012) and to those values reported in European background sites 0.5 to 60 ng m^{-3} (typically <10 ng m^{-3}) of Σ_{12}PAHs detected by Jaward et al. (2004b). The analysis of the wind from the surrounding weather stations shows that the

air masses affecting the area come from the west and north–northwest (see the SM, Figure S3), and therefore the surrounding industrial area, located in the southern of Bari (see the SM, Figure S1), is not expected to impact significantly on the urban area. Amodio et al. (2009) have also reported similar evidence in their own findings. In addition, advection to Bari during the entire passive sampling period was analyzed using Lagrangian modeling (HYSPLIT model using GFS meteorological inputs; Draxler and Rolph, 2003). Trajectories were released every 6 hours, at 100 m, and run for 24 hours back in time. Of the total 1 820 trajectories only 69 passed over the Taranto area. The results of the HYSPLIT output corroborate the negligible possible influence of emissions from the Taranto area (≤4% of air masses; Figure S7). Therefore, the PAH levels detected in this study might reflect the impact of diffuse emission sources, which are well known to be proportional to the population density and intensity of vehicular traffic. The city of Bari has a population of ~320 000, and a metropolitan area of ~1 million inhabitants, with an average population density of ~3 000 per km^2, which is as high as 18 000 per km^2 in the city center.

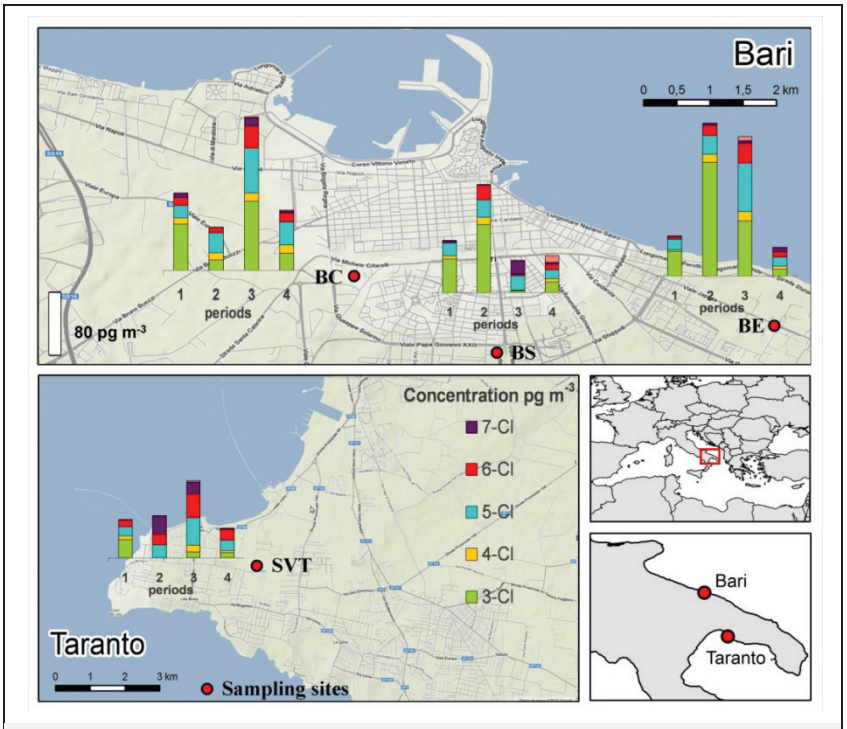

Figure 1. *Four periods concentrations (pg m^{-3}) of PCBs congeners in two cities of Puglia region in Southern Italy.*

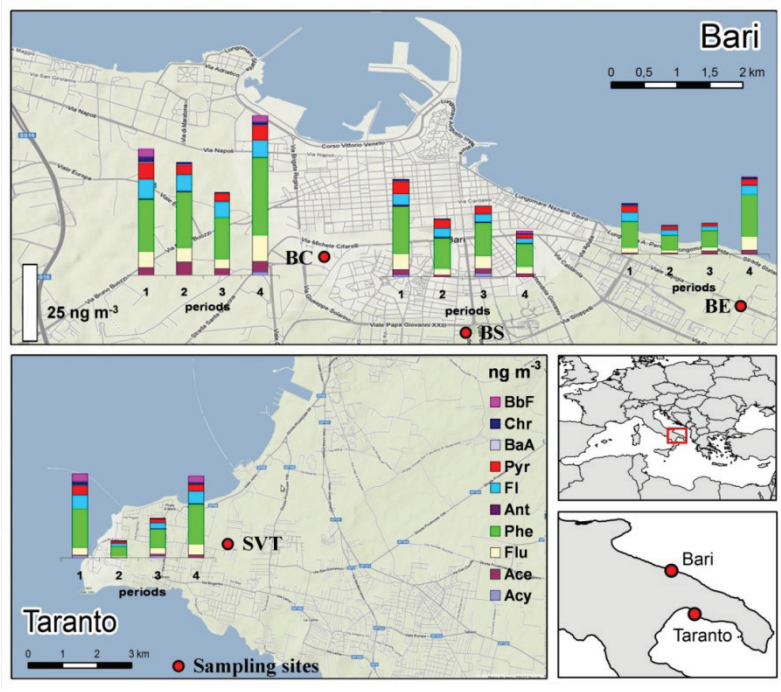

Figure 2. *Four periods concentrations (ng m^{-3}) of Total PAHs compounds in two cities of Puglia region in Southern Italy.*

The Bari urban center is characterized by high motor–vehicle traffic density (Amodio et al., 2009). Automobile exhaust is recognized as one of the main PAH contributors in urban areas (Hafner et al., 2005). Depending on the volatility of the individual compound, PAHs are transported either in gaseous form or bound to aerosol particle in the atmosphere. The gaseous state is predominant for the lighter molecular weight PAHs (2 to 4 rings), while the higher molecular weight compounds (more than 4 rings) are preferentially associated with particles (Jaward et al., 2004a).

The lower molecular weights PAHs (3– and 4–rings compounds) were detected in all the samples analyzed. However, higher molecular weights (5– and 6–rings) were not detected in any of the samples with the exception of B[b]F which only contribute ~0.3% of total PAHs, and was detected only during periods 1 and 4 (see the SM, Table S3). The PAH groups showed the following prevalence: 3–rings PAHs accounted for the (71±5)%, 4–rings for (29±5)%, and 5–rings for (0.3±1)% (Table 1, see the SM, Figure S8). The PAH pattern during the fourth sampling periods was dominated by phenanthrene (49±2)%, followed by fluorene (15±3)% and fluoranthrene (13±3)% (see the SM, Table S3 and Figure S8). The PAH pattern observed in this study is consistent with previous studies in the Tuscan region (Estellano et al., 2012), in Manila city, Philippines (Santiago and Cayetano, 2007), and across Europe (Jaward et al., 2004a).

Figure S9 shows the results of PCA analysis for PAHs during the four sampling periods. The first component and second component explained, respectively, 45% and 44% of the total variance in period 1; 74% and 24% period 2; 50% and 35% in period 3; and 79% and 16% in period 4 (see the SM, Figure S9). The main sources of PAHs in Italy are combustion in residential (51%), production processes (21%) and waste treatment (20%) (see the SM, Table S4). Similarly to PCBs, during the four sampling periods, the four sampling sites differ substantially from each other, highlighting the large variability between them.

3.3. Seasonal trends of PAHs and PCBs

Seasonal variations were observed at all the sampling sites for ΣPAHs (see the SM, Figure S4). The highest ΣPAH mean values (ng m^{-3}) were found during period 4 (autumn) (27±14) and period 1 (winter) (26±9), both showed similar mean values. The lower values were detected during period 3 (summer) (17±7) and period 2 (spring) (16±13) (Figure 2, see the SM, Figure S4). Bari center showed a seasonal variation in the ΣPAHs concentration (ng m^{-3}) of about two times higher during period 4 (autumn) (46) as compared to period 3 (summer) (25). A similar variability in concentrations was observed in Bari east ~two times higher during periods 4 (autumn) (23) as compared to period 2 (spring) (9) and by contrast in Bari south higher levels were detected during periods 1 (winter) (29) and 4 (autumn) (13). In San Vito Taranto, however, the differences in concentrations were about five times higher during periods 1 (winter) and 4 (autumn) (~23) as opposed to period 2 (spring) (5); therefore, the seasonality for this site was more marked. This pattern could be explained because during the warmer seasons (summer and spring), levels of PAHs are lower than the colder seasons (winter or autumn), probably due to the lower vehicular traffic, the lack of temperature inversion and no or less heating utilization (Jaward et al., 2004a).

Seasonal fluctuations in the air concentrations of $\sum_{26}$PCBs were also observed (see the SM, Figure S4), with the highest PCB values (pg m^{-3}) found during period 3 (summer) (116±77) and period 2 (spring) (100±64). The lower values were detected during period 1 (winter) (63±24) and period 4 (autumn) (45±22). The seasonal variation (pg m^{-3}) at Bari center was about three to five times higher between period 2 (200) and 3 (60), at Bari east between periods 2 (180) and 4 (30), at Bari south between period 2 (130) and 3 (40), and also at San Vito Taranto between periods 3 (90) and 4 (34). PCB air concentrations showed a seasonal trend with summer≈spring>winter≈autumn, contrasting PAHs the trend with autumn≈winter>summer≈spring. The PCB seasonal trends were similar to those reported by Melymuk (2012) in Toronto, Canada. This pattern is consistent with the temperature–driven re–emission of PCBs from secondary sources (e.g. soil) that results in a proportional increase in the lower molecular weight PCBs in air during the warmer months due to their greater volatility (Li et al., 2003).

3.4. Predicting air concentrations of PCBs and B[b]F using the Air Quality Modeling System "QualeAria"

A detailed description of the QualeAria modeling system and set up is presented in the SM, Text S3 (see also Figure S10). The AQMS is based on FARM that accounts for the main processes involving POPs: emissions, transport and dispersion, chemical transformations, partitioning (gas and aerosol phases), deposition (wet and dry). The version of FARM used in this study follows the assumptions implemented in the MSCE–POP model used by EMEP (Gusev et al., 2005) to simulate the fate of these pollutants in the atmosphere. The main goal of this modeling exercise is to check the capability of QualeAria to reproduce observed POPs concentrations in view of its further application to smaller horizontal scales. Its space resolution (12 km) permits us to gain an insight into POPs spatial distribution over the Italian territory; nevertheless, the increase of its horizontal resolution or its application at smaller domains is desirable in order to better reproduce smaller scale processes induced by local features such as topography, meteorology, emissions. An example of a smaller scale application can be found in Silibello et al. (2013) that describe the application of a similar AQMS to a Roman urban area (1 km horizontal resolution). In Mircea et al. (2012) and Silibello et al. (2012) a similar analysis can be found at national scale respectively for ozone and B[a]P, evidencing a good reproduction of the spatial and temporal structure of concentration levels. According to these results and to the above mentioned considerations about the main goal of the modeling exercise, we have limited the analysis to 5 PCBs congeners and B[b]F (the only HMW PAHs detected) that were simulated by the AQMS. Predicted air concentrations of PCBs congeners (–28, –105, –118, –153 and –180) and PAHs (B[a]P, B[k]F, B[b]F and I[l,2,3–cd]P), using QualeAria, are available for 2010 over the Italian peninsula (see the SM, Figure S11). In this study, results for the period from January 1st to March 28th 2010, that partially corresponds to period 4 of our study, were considered to check the capability of the adopted AQMS to reproduce observed levels at the monitoring sites located in the two cities in the Puglia region (see the SM, Table S1).

To be consistent with field measurements provided by PUF–PAS, computed concentrations were obtained from the entire gas and particulate phases (see the discussion in Section 2.3.). The B[b]F air concentration, calculated by QualeAria and averaged on the considered period, are spotty with the highest values located in major urban areas of the Italian Peninsula (Milan, Turin, Roma, Naples) and in the Puglia Region in Bari and Taranto areas (see the SM, Figure S11). These levels could be attributed to the contribution of elevated non–industrial combustion activities (e.g. domestic heating emissions) and to the PAH emissions in the main urban areas of the country (about 56%, see the SM, Table S4) with the exception of Taranto whose steel industries are the largest individual source of PAHs in the country according to the national emission inventory. PCBs air concentration fields exhibited a higher spread distribution through Italy with higher values around urbanized and industrialized areas (see the SM, Figure S11).

The comparison between observed (PUF–PAS) and predicted PCBs congeners (–28, –105, –118, –153 and –180) and B[b]F air concentrations, limited to the 4th period, is presented in the Figure 3. Two different approaches about PAS–PUF disk capability

to sample ambient particles were considered based on previous studies (see Section 2.3). The analysis of this figure evidences the good performance of AQMS with respect to PCBs using both approaches: the Pearson Correlation Coefficient (*r*) in both approaches is equal to 0.8 with a good statistical agreement ($p>0.05$). The performance is lower for B[b]F ($r=-0.6$) using both approaches. However, we observed a different behavior of the B[b]F concentrations using 10% (measured levels>predicted) rather than 100% (measured levels<predicted levels). These results could be explained by first considering the model uncertainties which are related to the estimation of domestic heating emissions and to the degradation of POPs in the particle–bound and gaseous phase in the atmosphere, including photodegradation that were not accounted for in the FARM, and also with the adopted spatial resolution (12 km x 12 km) that does not adequately take into account local effects (e.g. sources in the near range) that influence the observed levels at the monitoring sites. Secondly, the influence of PUF disk capability to sample the HMW PAHs, which apparently show two different accumulation results in the PUF disk, as was previously discussed in Section 2.3. Further research is needed in order to clarify the influences that the *R*–values can be subjected to under different sampler designs, gas–particle partitioning, deployment time, temperature, wind speed, and the specific characteristic of the sampling sites.

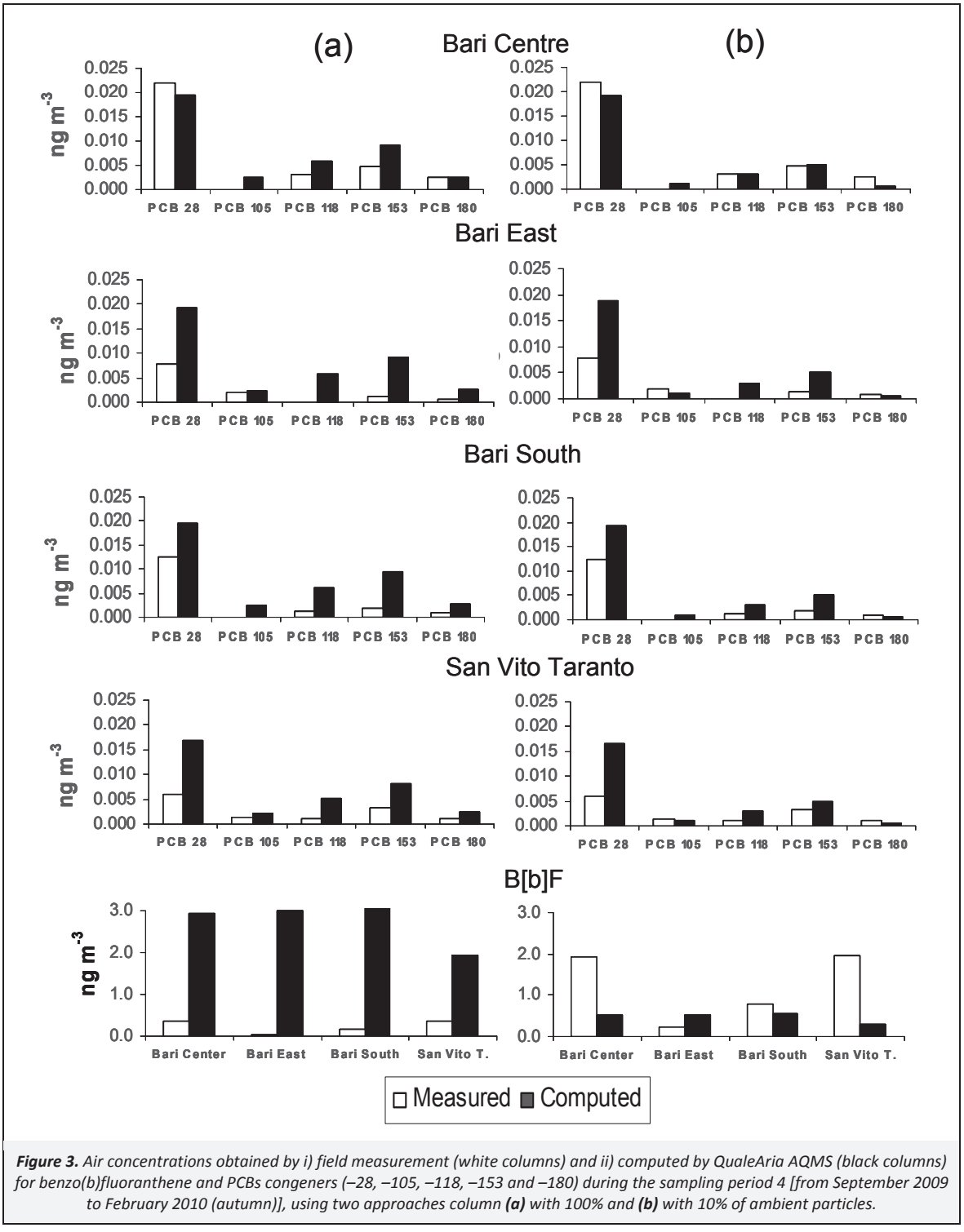

Figure 3. *Air concentrations obtained by i) field measurement (white columns) and ii) computed by QualeAria AQMS (black columns) for benzo(b)fluoranthene and PCBs congeners (–28, –105, –118, –153 and –180) during the sampling period 4 [from September 2009 to February 2010 (autumn)], using two approaches column* ***(a)*** *with 100% and* ***(b)*** *with 10% of ambient particles.*

4. Conclusions

This study reports the spatial and seasonal variation of PCBs and PAHs at four sampling sites in the Puglia Region, Italy, during one year of passive sampling. In the case of PCBs, the concentrations were lower than for other European urban sites and PCB patterns were dominated by low to middle molecular weight congeners at most of the sites; whereas for PAHs, levels in the air were similar to those reported throughout Europe and were dominated by phenanthrene. Both PCBs and PAHs showed seasonal variation in their concentrations, however with an opposite trend. Higher air concentrations of PCBs were detected during the warmer periods 3 (summer) and 2 (spring), and higher concentrations for PAHs during the colder periods 4 (autumn) and 1 (winter) and attributed to different types of sources for PCBs vs PAHs. The availability of modeled PCBs and PAHs concentration fields over the Italian peninsula has permitted us to check the capability of the adopted AQMS to realistically reproduce these pollutants. Since these fields are available for the 2010, the evaluation has been limited to period 4. The comparison between observed and predicted concentrations has evidenced a better performance of the AQMS for PCB congeners than for PAHs probably due to the considered spatial resolution (12 km x 12 km) that does not adequately take into account local processes (topography, meteorology, emissions) that influence the observed concentrations. These promising results confirm the need for an integrated approach to investigate air pollution issues based on measurements and modeling techniques. Moreover, the wider use of passive air samplers together with the application of models at a higher spatial resolution will improve our knowledge on the fate of these pollutants. It will also allow for a wider evaluation of model results that will set the basis towards proper emission control strategies to reduce the exposure of the population to these pollutants.

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Supporting Material Available

Text S1 is the description of the sampling sites. Text S2 reported the PCBs and PAHs target/qualified ions, and the instrumental conditions. Text S3 reported the modeling set up. Figure S1 is the Map of sampling sites. Figure S2 is a schematic representation of the PUF and a photo. Figure S3 showed the wind direction at Bari Palese all year. Figure S4 is the box and whisker plot. Figure S5 is the PCBs congeners composition (%) during the 4 periods. Figure S6 shows the score plot for PCA applied to PCBs congeners. Figure S7 showed the sum of 24–hour backward trajectories obtained from the HYSPLIT model. Figure S8 is the PAHs compound composition (%) during the 4 periods. Figure S9 is the score plot for PCA applied to PAHs. Figure S10 gives the diagram of the AQMS QualeAria, and the QualeAria background and national domains. Figure S11 reports the maps of PCBs congeners (28, 105, 118, 153 and 180) and B[b]F average concentrations computed by the AQMS over Italy. Table S1 provides sampling sites information. Table S2 showed the air concentrations (pg m^{-3}) of PCBs individuals congeners, the MDL and air volumes (V_{AIR}, m^3). Table S3 showed the air concentrations (pg m^{-3}) of individuals PAHs a MDL and V_{AIR}, m^3. Table S4 gives the contributions of different activities to Italian PAHs emissions (ton/year). This information is available free of charge via the Internet at http://www.atmospolres.com.

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